

Weitz and Ladd Reply: The authors of the previous Comment [1] make the interesting observation that the hard-sphere pair distribution evaluated at contact, $\chi(\phi)$, adequately represents the volume fraction (ϕ) dependence of both the inverse self-diffusion coefficient, $D_S(\phi)/D_0 \approx \chi^{-1}(\phi)$, and the suspension viscosity, $\eta(\phi)/\eta_0 \approx \chi(\phi)$; here $D_0 = k_B T / 6\pi\eta_0 a$ is the self-diffusion coefficient of an isolated particle of radius a , and η_0 is the viscosity of the suspending fluid. Physically, this observation suggests that long-range hydrodynamic interactions are not important; instead direct interactions between neighboring particles dominate. However, there is abundant evidence that hydrodynamic interactions do determine the transport coefficients in colloidal suspensions; experimental measurements of both the diffusion coefficient and the viscosity are quantitatively reproduced by theoretical and numerical calculations based solely on hydrodynamic interactions [2] with no direct interparticle forces. Thus, while the apparent agreement of $\chi(\phi)$ with the data is appealing, the implications of this observation for the underlying physics must be examined carefully.

The close correspondence between $D_S(\phi)/D_0$ and $\eta_0/\eta(\phi)$, noted in Ref. [1], can be understood in terms of a mean-field theory. Because of the *long-range* hydrodynamic interactions, a diffusing sphere interacts with other spheres as if they were a continuum fluid, stiffened by the suspension viscosity, $\eta(\phi)$, rather than the fluid viscosity, η_0 . However, this mean-field approximation is not exact. Accurate numerical calculations of $D_S(\phi)$ and $\eta(\phi)$ indicate that there is a distinct difference between them; the product $D_S(\phi)\eta_0/D_0\eta(\phi)$ varies monotonically between 1 at low volume fractions and 1.36 at $\phi = 0.45$ [2]. Furthermore, a careful examination of the experimental data indicates that there is a difference between $D_S(\phi)/D_0$ and $\eta_0/\eta(\phi)$ that is greater than the considerable experimental scatter; this difference is better described by the numerical calculations than by a single function, $\chi^{-1}(\phi)$.

An important feature of the argument in the previous Comment [1] is the presence of two distinct time scales in a colloidal suspension. They are the viscous time, $\tau_\nu = \rho a^2 / \eta_0$ (ρ is the fluid density), which sets the time scale for the evolution of hydrodynamic interactions, and the diffusion time, $\tau_D = a^2 / D_0$, which sets the time scale for changes in particle configuration. The key experimental result is that, for $t_\nu < t < 100t_\nu \ll \tau_D$, the time-dependent self-diffusion coefficient at all volume fractions, $H(t, \phi) = \langle \Delta R^2(t) \rangle / 6D_0 t$, can be scaled to a single master curve $C(\phi)H_0(t/\tau(\phi))$ [3]. The function H_0 describes the time-dependent self-diffusion coefficient of an isolated Brownian sphere. The experimental data [3] scale most accurately when the amplitude is scaled to the self-diffusion coefficient [$C(\phi) = D_S(\phi)/D_0$], and the time scale is scaled to the inverse viscosity [$\tau(\phi)/\tau_\nu = \eta_0/\eta(\phi)$]. The scaling obtained with a single function, either $D_S(\phi)/D_0$, $\eta_0/\eta(\phi)$, or some functions in between

[such as $\chi^{-1}(\phi)$] is clearly less good. Other experimental data, obtained for much shorter items (up to $4\tau_\nu$) [4], were insufficient to distinguish this scaling from other possibilities. Self-diffusion data from computer simulations of hydrodynamically interacting spheres [5] can also be scaled in the same way as the experiments. Unlike the experiments, the scaling of the computer data is improved if both the time and amplitude are scaled by a single coefficient [6]; however, this coefficient is $D_S(\phi)/D_0$, rather than $\eta_0/\eta(\phi)$. These small discrepancies between simulation and experiment are more pronounced at longer wavelengths, where the hydrodynamic interactions between neighboring particles are more significant [7]. We think that these differences in apparent relaxation time may actually reflect an extra relaxation mechanism in the laboratory experiments that operates mainly at long wavelengths and at short times. One possibility is additional momentum transfer caused by propagating sound waves [7], which was not included in the simulations. Another possibility is that the short-time diffusion is affected by direct interparticle forces [6]; this would be consistent with the suggestion of Cohen and de Schepper [1]. Nevertheless, we emphasize that the transport properties of colloidal suspensions are not determined primarily by direct interparticle interactions; however, they can be quantitatively explained by hydrodynamic interactions alone.

This work was partially supported by NASA, the U.S. Department of Energy, and Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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Received 18 April 1995

PACS numbers: 82.70.Kj, 05.40.+j, 66.20.+d, 82.70.Dd

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